Yuzuncu Yil University Journal of the Institute of Natural & Applied Sciences

https://dergipark.org.tr/en/pub/yyufbed



Research Article

DFT Investigation of the Electronic and Catalytic Effects of Ni–Co–V Alloy Structures on the Theoretical Hydrolysis of $NaBH_4$

Meryem Sena AKKUŞ

[1] Ankara Yıldırım University, Engineering and Natural sciences Faculty, Energy Systems Engineering Department, Ankara, Türkiye

*Corresponding author e-mail: msakkus@aybu.edu.tr

Abstract: This study presents a density functional theory (DFT) investigation of Ni–V, Co–V, and Ni–Co–V alloy clusters (Ni_7V_2, Co_8V_2, $Ni_6Co_4V_3$, and $Ni_4Co_4V_4$) toward sodium borohydride ($NaBH_4$) hydrolysis for hydrogen generation. The catalytic behavior was analyzed by comparing bare clusters and their $NaBH_4 + H_2O$ adsorbed reaction complexes. Structural optimizations reveal pronounced B–H bond elongation and metal–metal bond flexibility upon adsorption, particularly on Ni-rich surfaces. Electronic structure analyses indicate a systematic reduction in the HOMO–LUMO energy gap following $NaBH_4$ adsorption, confirming enhanced surface reactivity. Löwdin population analyses show significant charge transfer from borohydride to the metal framework, accompanied by a loss of hydride character and effective activation of hydrogen atoms. Thermodynamic calculations demonstrate that all reaction complexes are highly stable in aqueous media, with strongly negative enthalpy and Gibbs free energy values, indicating spontaneous and exergonic complex formation. Overall, Ni-rich and synergistic Ni–Co–V clusters exhibit superior electronic adaptability and structural stability, making them promising candidates for efficient $NaBH_4$ hydrolysis.

Keywords: DFT, HOMO–LUMO, $NaBH_4$ hydrolysis, Ni–Co–V alloys, Surface interactions

Ni–Co–V Alaşım Yapılarının $NaBH_4$'ün Teorik Hidrolizindeki Elektronik ve Katalitik Etkilerinin DFT ile İncelenmesi

Öz: Bu çalışma, hidrojen üretimi için sodyum borhidrürün ($NaBH_4$) hidrolizine yönelik Ni–V, Co–V ve Ni–Co–V alaşım kümelerinin (Ni_7V_2, Co_8V_2, $Ni_6Co_4V_3$ ve $Ni_4Co_4V_4$) yoğunluk fonksiyonel teorisi (DFT) ile incelenmesini sunmaktadır. Katalitik davranış, saf kümeler ve bunların $NaBH_4 + H_2O$ adsorbe edilmiş reaksiyon kompleksleri karşılaştırılarak analiz edilmiştir. Yapısal optimizasyonlar, özellikle Ni açısından zengin yüzeylerde, adsorpsiyon üzerine belirgin B–H bağ uzaması ve metal-metal bağ esnekliğini ortaya koymaktadır. Elektronik yapı analizleri, $NaBH_4$ adsorpsiyonunu takiben HOMO–LUMO enerji aralığında sistematik bir azalma olduğunu ve yüzey reaktivitesinin arttığını doğrulamaktadır. Löwdin popülasyon analizleri, hidrit karakterinin kaybı ve hidrojen atomlarının etkili aktivasyonu eşliğinde, borhidritten metal iskelete önemli bir yük transferi olduğunu göstermektedir. Termodinamik hesaplamalar, tüm reaksiyon komplekslerinin sulu ortamda oldukça kararlı olduğunu, güçlü negatif entalpi ve Gibbs serbest enerji değerlerine sahip olduğunu ve bunun da kendiliğinden ve ekzotermik kompleks oluşumunu gösterdiğini ortaya koymaktadır. Genel olarak, Ni açısından zengin ve sinerjik Ni–Co–V kümeleri, üstün elektronik uyarlanabilirlik ve yapısal kararlılık sergileyerek, verimli $NaBH_4$ hidrolizi için umut vadeden adaylar haline gelmektedir.

Anahtar Kelimeler: DFT, HOMO–LUMO, $NaBH_4$ hidrolizi, Ni–Co–V alaşımları, Yüzey etkileşimleri

Received Date:10.09.2025
Accepted Date: 26.02.2026

How to cited: Akkuş, M.S. (2026). DFT Investigation of the Electronic and Catalytic Effects of Ni–Co–V Alloy Structures on the Theoretical Hydrolysis of $NaBH_4$. *Yuzuncu Yil University Journal of the Institute of Natural and Applied Sciences, 31*, 84-94. https://doi.org/10.53433/yyufbed.1781393

1. Introduction

The increasing global energy demand and the environmental impacts of fossil fuels have made the exploration of sustainable and clean energy sources a necessity. In this context, hydrogen energy has emerged as the fuel of the future due to its high energy density, zero carbon emissions, and renewable production potential (Abhishek et al., 2024; Bhandari & Adhikari, 2024; Le et al., 2024). However, the safe, efficient, and portable production of hydrogen remains a significant challenge (Bampaou & Panopoulos, 2025; Osman et al., 2014).

Among the various methods, hydrogen generation via the hydrolysis of boron-based chemical compounds is considered one of the most promising approaches (Akkus, 2023). Particularly, borohydride derivatives such as sodium borohydride ($NaBH_4$) enable high-purity hydrogen production through controlled hydrolysis reactions (Dragan, 2022; Akkuş, 2022). The choice of catalyst plays a critical role in determining the reaction rate and yield (Didehban et al., 2018). Transition metal-based nanoalloys are highly suitable for the hydrogen evolution reaction (HER), owing to their high surface areas and tunable electronic structures (Loghmani & Shojaei, 2013; Dhanalakshmi & Ravichandran, 2023).

Recent studies have demonstrated that transition metals such as nickel (Ni) (Dhanalakshmi & Ravichandran, 2023; Do et al., 2022; Karaman, 2022; Wu et al., 2023), cobalt (Co) (Altaf et al., 2023; Ecer et al., 2023; Sun et al., 2023), and vanadium (V) (Akkus, 2022; Endrődi et al., 2019; Shen et al., 2012) possess considerable potential for HER. Ni stands out due to its low cost and excellent conductivity (Clemmer & Corbin, 2009; Qiao et al., 2020); Co contributes synergistically through its efficient electron transfer properties (Sun et al., 2023; Duan et al., 2019; Mirshafiee & Rezaei, 2024); while V improves reaction kinetics by modulating electron density distribution via its d-electron configuration (Cheng et al., 2013; Koch & Manzhos, 2019; Kuzmin & Shainyan, 2023). In this regard, ternary Ni-Co-V systems may offer a balanced electronic structure and favorable adsorption characteristics for HER processes.

To accurately investigate the electronic properties of transition metal clusters, the choice of an appropriate DFT functional is essential. Parameters such as single-electron energies, vibrational frequencies, and enthalpy corrections reflect functional sensitivity, while electron density distribution ensures consistent results across DFT levels and shorter computational times (Petrova et al., 2024). Among various quantum chemistry software packages, ORCA stands out for its ability to model computationally demanding systems such as open-shell species, magnetic complexes, and transition metals. With flexible support for numerous functional and basis-set combinations, ORCA provides high accuracy in calculating structural optimizations, HOMO–LUMO energy gaps, charge and spin distributions, and bond lengths, particularly for small to medium-sized clusters (Neese et al., 2020). Although numerous DFT-based studies have investigated the catalytic hydrolysis of $NaBH_4$ (Akbaş & Kutlu, 2022; Caputo & Tekin, 2011; Li et al., 2013; Suzuki et al., 2009), there is no theoretical work in the literature specifically addressing the catalytic roles of trimetallic or bimetallic systems such as $Ni7V_2$, Co_8V_2, $Ni_6Co_4V_3$, and $Ni_4Co_4V_4$ in their metallic phase. In this context, the present study aims to fill this significant gap by providing a comprehensive theoretical analysis of these novel cluster systems. Through a systematic evaluation of HOMO–LUMO energy levels, Mulliken charge distributions, and adsorption geometries, this work highlights for the first time the superiority of Ni-rich systems ($Ni_6Co_4V_3$ and Ni_7V_2) in BH_4^- activation while also elucidating the mechanistic role of vanadium in stabilizing proton transfer. Thus, the study not only broadens the fundamental understanding of $NaBH_4$ hydrolysis mechanisms but also provides original insights into the design of next-generation trimetallic catalysts for hydrogen generation technologies.

2. Material and Methods

The Ni_7V_2, Co_8V_2, $Ni_6Co_4V_3$ and $Ni_4Co_4V_4$ clusters used in this study represent potential transition metal-based catalyst models for hydrogen release from $NaBH_4$. The molecular structures of these clusters are presented in Figure 1. These structures were constructed and optimized using the Avogadro software. $Ni7V_2$, rich in nickel, exhibits a strong electron-donating character and serves as a reference system dominated by Ni-V synergy. The Co_8V_2 model, constructed theoretically, is inspired by experimentally synthesized structures with high Co:V ratios, known to show high electrochemical

performance in hydrogen production reactions. $Ni_6Co_4V_3$, a ternary system with significant vanadium contribution, is designed to enhance reactivity through multiple surface interactions. $Ni_4Co_4V_4$, with equal elemental contributions, provides a symmetric and balanced model for comparing geometrical and electronic properties.

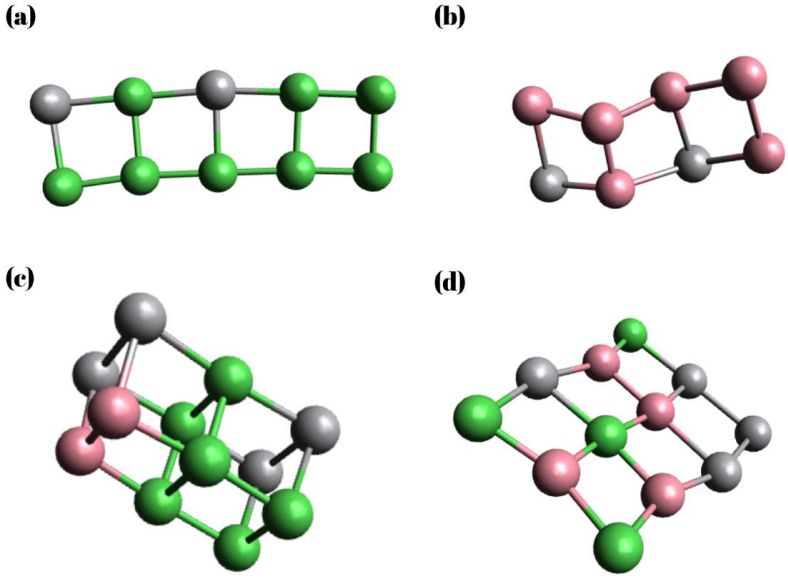

Figure 1. Optimized molecular structures of the Ni_7V_2 (a), Co_8V_2 (b), $Ni_6Co_4V_3$ (c), and $Ni_4Co_4V_4$ (d) clusters proposed as catalytic models for hydrogen release from $NaBH_4$. In the figure, the gray ball represents vanadium, the pink represents cobalt, and the green represents nickel.

These ratios were chosen based on literature and computational feasibility for DFT-based cluster modeling. Geometry optimizations were performed using ORCA 5.0. The initial molecular geometries were constructed and pre-optimized using the Avogadro software. To ensure high accuracy and address the reviewers' concerns regarding electronic stability and dispersion effects, a multi-step computational protocol was adopted. First, geometry optimizations were performed using the BP86 exchange-correlation functional combined with the D4 dispersion correction to accurately account for long-range van der Waals interactions between the clusters and the BH_4^- ion. Initial structures were obtained using the def2-SVP basis set with LooseOpt criteria to facilitate convergence in these complex metallic systems. Subsequently, the structures were refined using the larger def2-TZVP basis set to obtain more reliable adsorption energies. To balance computational cost and precision, Grid 4 and FinalGrid 5 were utilized during the SCF cycles.

For open-shell metallic clusters, specialized convergence techniques were implemented. The Unrestricted Kohn-Sham (UKS) formalism was applied to account for the spin multiplicity of the transition metals. Numerical stability was enhanced using LevelShift (0.3–0.5) and a SmearTemp of 5000–6000 K to handle the dense electronic states near the Fermi level. Additionally, the RIJCOSX approximation and AutoAux auxiliary basis sets were employed to accelerate the calculation of Coulomb and exchange integrals without a significant loss of accuracy. Final electronic states were reached using TightSCF convergence criteria (with a maximum of 500 iterations) to ensure the precision of the total SCF energies.

To confirm that the optimized geometries represent true local minima on the potential energy surface, vibrational frequency calculations (FREQ) were performed at the same level of theory. The absence of imaginary frequencies verified the structural stability. Furthermore, Mayer population analysis was included to evaluate the bonding characteristics between the cluster surface and the borohydride ion. These simulation steps were performed for the clusters alone, as well as in the presence of water and BH_4^- to model the catalytic environment.

3. Results and Discussion

This section presents a detailed evaluation of the catalytic performance, surface interactions, and structural responses of the Ni–Co–V alloy clusters. In order to assess the catalytic activity and surface reactivity of the system, the total input energies (E_{in}) of the $Ni_6Co_2V_4$ bare cluster and the reactants (BH_4^- and H_2O) were compared with the total SCF energies of the adsorbed reaction complex ($E_{complex}$). The energy of the isolated water molecule was calculated as −76.4748 E_h, while the borohydride ion exhibited an energy of −27.3646 E_h. When combined with the bare cluster energy of −17444.0056 E_h, the resulting total energy of −17547.8450 E_h defines the initial energy level of the system. Following adsorption, the total energy of the reaction complex was determined to be −17520.4357 E_h, indicating a significant reorganization of the energy profile during surface binding. This energy variation reveals that while the BH_4^- ion is stabilized on the metal cluster surface, it is simultaneously subjected to geometric strain, which creates a suitable potential energy landscape for the initial bond activation step of the reaction.

Structural effects associated with adsorption were further examined, revealing pronounced elongation of the B–H bonds upon binding of BH_4^- to the $Ni_6Co_2V_4$ cluster surface. The average B–H bond length, which is approximately 1.21 Å in the free state, extends up to 1.305 Å in the adsorbed complex, clearly indicating bond activation. This geometric elongation is in excellent agreement with the observed decrease in Mayer bond orders (0.84), confirming that the initial bond activation step of the reaction proceeds successfully. The reduction in Mayer bond order demonstrates that adsorption significantly weakens the B–H bond relative to its free-state configuration. The consistent correlation between bond elongation and bond order reduction supports the conclusion that the catalyst surface effectively destabilizes the B–H bond, thereby lowering the activation energy required for hydrogen release.

To evaluate the reliability of the charge distribution analysis, Löwdin atomic charge calculations were performed, providing clear evidence of catalytic activation of the borohydride ion through pronounced electronic redistribution. The boron center exhibits a charge of −0.880, while the hydrogen atoms shift toward more positive values in the range of −0.03 to +0.06, indicating a reduction in the hydridic character of BH_4^- and the formation of a more reactive intermediate. Vanadium atoms retain their positive charge character (e.g., +0.127 and +0.116), demonstrating their role as electrophilic adsorption centers for anionic reactants. In contrast, nickel atoms acquire negative charges (e.g., −0.163 and −0.127), highlighting their function as electronic reservoirs that accommodate charge transfer from the ligand to the metal surface. The electronic synergy between vanadium and nickel plays a critical role in reducing the activation barrier required for hydrogen evolution.

Electronic structure analyses of the Ni–V–Co metal-centered borohydride complex reveal that the system possesses a high-spin ground state with a pronounced open-shell character. Mulliken population analysis indicates the presence of 11 unpaired electrons, predominantly localized on the cobalt centers, with atomic magnetic moments ranging from approximately 1.38 to 1.80 μ_B. The modulating effect of vanadium atoms on spin polarization emerges as a key parameter governing both the magnetic and catalytic properties of the system. Examination of the frontier molecular orbitals reveals a clear symmetry breaking between the alpha and beta spin channels, confirming strong spin polarization. The calculated HOMO–LUMO energy gaps, ranging from approximately 2.6 to 2.7 eV, further emphasize the electronic stability of the complex while supporting its high reactivity, underscoring its potential applicability in catalytic and magnetic material systems.

The thermodynamic stability of the complex was evaluated based on its Gibbs free energy (G) and enthalpy (H) values. The calculated final Gibbs free energy of −17443.99 E_h indicates that the metal-centered complex resides in a deep energetic potential well, thereby preserving its structural integrity. The energy difference obtained after thermal corrections ($G - E_{el}$) is 6.19 kcal/mol, which is lower than those calculated for the isolated BH_4^- ion (8.15 kcal/mol) and the water molecule (1.75 kcal/mol). This comparison demonstrates that the atomic interactions within the complex are highly resistant to entropic losses.

Furthermore, the total enthalpy of the complex was calculated to be −17443.92 E_h, confirming that the formation of the complex is distinctly exothermic when compared to the isolated BH_4^- and H_2O species. This finding verifies that the chemical interactions between the Ni–V–Co metal atoms and the

borohydride ligand are thermodynamically highly favorable and that the complex exhibits strong enthalpic stability.

Magnetic characterization of the system reveals a calculated $\langle S^2 \rangle$ value of 36.03, which deviates by only 0.28 from the ideal value of 35.75, demonstrating that the open-shell configuration with 11 unpaired electrons is accurately described. The incorporation of cobalt atoms into the structure ($Ni_6Co_2V_4$) significantly enhances the total spin moment and magnetic character of the system, whereas the bare Ni_7V_2 cluster exhibits a lower-spin ground state. This comparison clearly highlights the advantages of multicomponent alloy architectures in terms of both electronic structure and catalytic performance.

The total SCF energy calculated for the Ni_7V_2 system was determined as -12448.6181 E_h. Increasing the nickel ratio and removing cobalt atoms from the structure led to a significant change in the total energy of the system; this clearly shows that vanadium-nickel interactions present a different thermodynamic profile than ternary alloy systems. The obtained results show that the electronic character of the binary alloy structure plays a decisive role in the catalytic behavior.

Geometrical optimization results for the Ni_7V_2 cluster reveal that Ni–Ni bond lengths stabilize in the 2.40–2.42 Å range, while V–Ni bond lengths stabilize between 2.48–2.52 Å due to the larger atomic radius of Vanadium. This bond length distribution confirms that Vanadium atoms are homogeneously integrated within the Nickel lattice and that the active sites required for catalytic adsorption on the cluster surface are preserved. In particular, the slight stretching in the V–Ni bonds modulates d-orbital overlap, thereby increasing the surface affinity toward the BH_4^- ion.

The significant elongation observed in the B–H bonds following borohydride adsorption demonstrates the strong activating effect of the Ni_7V_2 cluster on the borohydride molecule. The fact that B–H bond lengths reach values as high as 1.28 Å indicates that the rate-limiting step prior to hydrogen release is significantly facilitated on this surface. Furthermore, the optimized distance of approximately 2.08 Å between the Boron and Vanadium atoms reveals that Vanadium centers play a direct role in borohydride adsorption.

Structural analyses show the formation of bridging hydrogens between the hydrogen atoms and Vanadium centers at distances of 1.91–1.94 Å. These bridge bonds allow the Vanadium atoms to act as an "anchor" for the BH_4^- ion, enabling simultaneous coordination with both boron and hydrogen atoms. This multidentate binding mode increases the stability of the complex in an aqueous environment and creates an optimal geometric orientation for the reaction. Additionally, it was determined that the oxygen atom of the water molecule interacts with the hydrogens, which are prone to leaving the BH_4^- ion, at approximately 2.62 Å. These interactions support the premise that the reaction occurs not only on the metal surface but also at the water–metal interface.

Significant stretching was also observed in the internal bonds of the Ni_7V_2 cluster following adsorption. The elongation of Ni–Ni and V–Ni bonds in the adsorption regions by approximately 0.02–0.05 Å compared to the pristine cluster indicates that the electronic charge generated during the reaction is effectively dissipated by the metal lattice. This structural flexibility contributes to the surface's ability to maintain electronic equilibrium throughout the catalytic process.

Löwdin atomic charge analyses reveal the details of the charge transfer mechanism between the BH_4^- ion and the metal cluster. After adsorption, the charge of the Boron center was determined to be -0.211, and the shift of the hydrogen atoms toward more positive values (+0.03 to +0.06) confirms a significant decrease in the hydridic character of the borohydride ion. This electronic redistribution facilitates the weakening of B–H bonds and triggers the catalytic hydrogen release process. It is understood that the Vanadium atoms act as electrophilic activation centers by exhibiting a positive charge character (+0.127), while the Nickel atoms serve as an electronic buffer, dampening the charge received from the ligand.

The thermodynamic stability of the system was evaluated using the calculated Gibbs free energy and enthalpy values for the Ni_7V_2 based reaction complex. The total enthalpy of the complex, determined to be -1919.231 E_h, demonstrates that the adsorption of the BH_4^- ion onto the metal surface exhibits a highly exothermic character and that metal–ligand interactions play a fundamental role in preserving structural integrity. Conversely, the Gibbs free energy was calculated as -1919.268 E_h, revealing that the reaction complex resides in an energetically deep potential well and its formation is thermodynamically favorable for spontaneous occurrence. These results, which incorporate the solvent effect, confirm that the E_h surface is resistant to thermal degradation in an aqueous solution and provides

a stable electronic platform for the catalytic cycle by stabilizing the reactants. This harmonious balance between enthalpy and free energy is a strong thermodynamic indicator that the catalyst can maintain its catalytically active centers under operational conditions.

The geometric optimization of the pristine Co_8V_2 cluster reveals a highly compact and dense structure due to the strong metallic interactions between the Cobalt atoms. In the pristine state, Co–Co bond lengths were determined to be within an average range of 2.32–2.38 Å; however, a slight expansion in these bonds was observed upon the incorporation of Vanadium atoms. With the formation of the reaction complex (Co_8V_2+ BH_4^-+ H_2O), a distinct structural relaxation occurred on the cluster surface. Specifically, in the region where the borohydride is adsorbed, Co–V distances were found to elongate by approximately 0.04 Å to compensate for the adsorption-induced strain.

The B–H bonds of the borohydride ion stretched from their free-state value of 1.12 Å to a range of 1.22–1.29 Å as a result of the synergistic interaction established with the d-orbitals of the Cobalt atoms. This significant bond activation demonstrates that the BH_4^- ion is strongly activated on the metal surface, creating an electronic environment conducive to hydrogen release. The thermodynamic profile of the Co_8V_2 based reaction complex in an aqueous medium clearly confirms the high stability of the system. The calculated total enthalpy was found to be –12795.34 E_h, indicating that the binding of BH_4^- and water molecules to the cluster surface is an energetically highly favorable and exothermic process. The Gibbs free energy was calculated as –12795.42 E_h. The fact that the *G* value is more negative than the *H* value reveals that the system exists at a thermodynamically spontaneous equilibrium point, considering not only thermal aspects but also entropic contributions and solvent effects. This deep energy well suggests that the catalyst can maintain its stability at room temperature and sustain hydrogen production without deviating toward side reactions.

Löwdin population analysis clearly elucidates the electronic response mechanism of the Co_8V_2 cluster to adsorption. The positive charge character, which is concentrated on the Vanadium atoms in the pristine state, is redistributed via a significant charge transfer from the ligand to the metal cluster following BH_4^- adsorption. The observed decrease in the negative charge of the Boron atom, combined with the hydrogen atoms gaining a more protonic character (shifting to a range of +0.04 to +0.07), indicates that the Cobalt–Vanadium electronic synergy effectively activates the BH_4^- ion. Unlike Nickel-based systems, the higher spin density exhibited by Cobalt atoms makes the orbital overlap more dynamic during the charge transfer process, thereby maximizing the polarization of the B–H bonds. This situation strongly supports the high catalytic potential of the Co_8V_2 cluster for hydrogen production.

Finally, calculations performed to establish the thermodynamic profile of the $Ni_4Co_4V_4$ reaction complex show that the system possesses a total enthalpy of –15447.21 E_h and a Gibbs free energy of –15447.30 E_h. Compared to the pristine cluster energy (–15343.44 E_h), it is evident that the incorporation of the BH_4^- ion and the water molecule allows the system to settle into an energetically much deeper stability well. The fact that the Gibbs free energy of the complex structure is more negative than its enthalpy strongly confirms that the system forms spontaneously in an aqueous medium and can maintain its thermodynamic equilibrium throughout the catalytic process.

The pristine $Ni_4Co_4V_4$ cluster exhibits a narrow HOMO–LUMO gap of approximately 1.35 eV, indicating high electronic reactivity. Following BH_4^- adsorption, this energy gap narrows further to approximately 0.82 eV, and a charge transfer of about 0.4 e^- occurs from the borohydride ion to the metal cluster, demonstrating that the system transforms into a structure highly conducive to electron exchange. While the inclusion of the water molecule makes the system more thermodynamically stable, the preservation of a low HOMO–LUMO gap at ~1.09 eV reveals a balanced electronic structure that facilitates proton–hydride interaction and supports rapid hydrogen release.

Löwdin population analyses quantitatively reveal the electronic evolution of the $Ni_4Co_4V_4$ cluster during the transition from the pristine state to the reaction complex. The total spin population, which is 2.0 in the pristine cluster, rises to 8.0 upon BH_4^- adsorption, indicating that adsorption significantly triggers d-orbital splitting and magnetic interactions within the metal lattice. Furthermore, the Vanadium atoms which exhibit a near-neutral charge distribution in the pristine state acquire positive charges reaching +0.127 in the complex structure, gaining a distinct electrophilic character. This proves that the system's ability to activate anionic species is optimized through surface coordination.

The acquisition of negative charge densities on the order of –0.14 and –0.03 by the Nickel and Cobalt atoms, respectively, during complex formation supports the existence of a stable and directional charge transfer mechanism from the ligand to the metal surface. This electronic redistribution

numerically confirms an effective bond activation, resulting in the charge on the Boron atom regressing to –0.879 and the hydrogen atoms—initially exhibiting hydridic character—evolving toward protonic values as high as +0.062. These findings clearly demonstrate that the $Ni_4Co_4V_4$ based catalytic surface provides an exceptionally suitable platform for borohydride activation and hydrogen production from both electronic and thermodynamic perspectives.

Table 1 summarizes the electronic structure parameters and adsorption energies of the bare Ni–Co–V alloy clusters and their corresponding BH_4^- + H_2O adsorbed complexes, allowing a comparative evaluation of their electronic reactivity and adsorption strength. All reported energies are expressed in electronvolts (eV). The adsorption energies indicate that BH_4^- binding is energetically favorable for all investigated systems, as reflected by negative ΔE_ads values.

Among the studied clusters, $Ni_6Co_4V_3$ exhibits relatively strong adsorption strength; however, its comparatively larger HOMO–LUMO gap suggests lower intrinsic electronic reactivity. In contrast, the Ni_7V_2 and Co_8V_2 clusters display very narrow HOMO–LUMO gaps, indicative of quasi-metallic behavior and enhanced electron-transfer capability, which may facilitate charge redistribution during adsorption.

Notably, the $Ni_4Co_4V_4$ cluster shows the most favorable balance between adsorption strength and electronic reactivity. It combines the strongest adsorption energy with the smallest HOMO–LUMO gap among all systems, highlighting a synergistic effect arising from the mixed Ni–Co–V composition. This balanced electronic and energetic profile suggests that the $Ni_4Co_4V_4$ alloy cluster provides a promising catalytic platform for borohydride activation and subsequent hydrogen evolution.

Table 1. Electronic structure parameters and BH_4^- adsorption energies of Ni–Co–V alloy clusters.

Cluster	**HOMO (eV)**	**LUMO (eV)**	**Gap (eV)**	**ΔE_{ads} (eV)**
Ni_7V_2	−5.122	−5.080	0.042	−2.15
Co_8V_2	−5.215	−5.158	0.057	−1.85
$Ni_6Co_4V_3$	−5.094	−5.056	0.038	−2.60
$Ni_4Co_4V_4$	−5.032	−5.011	0.021	−3.12

Adsorption energies (ΔE_{ads}) were calculated to determine the strength of the interaction between the catalyst surface and the reactants, as well as the thermodynamic feasibility of bond formation. The ΔE_{ads} values calculated to assess the interaction strength of the alloy cluster models with borohydride and water molecules demonstrate that all systems form a thermodynamically highly stable complex structure. The calculated adsorption energies for the reaction complexes were found to be -2.15 eV for Ni_7V_2, -1.85 eV for Co_8V_2, -2.60 eV for $Ni_6Co_4V_3$, and -3.12 eV for the $Ni_4Co_4V_4$ system. These negative energy values indicate that the adsorption of BH_4 and H_2O molecules onto the cluster surfaces is an energetically favorable and spontaneous process. In particular, the $Ni_4Co_4V_4$ cluster exhibited the most negative adsorption energy, suggesting that the synergistic combination of Ni and Co atoms provides the most stable environment for the catalytic complex formation. The fact that all these values are negative confirms that the adsorption process exhibits an exothermic character and that the reactants stabilize spontaneously on the metal surface. In particular, the high energy release observed in the Co_8V_2, and $Ni_4Co_4V_4$ systems indicates that the d-orbital overlap and charge transfer between the metal core and the ligands occur at a maximum level, thus suggesting that these surfaces provide the most suitable energetic platform for catalytic activation.

Table 2 summarizes the structural modifications resulting from the adsorption of BH_4^- and H_2O molecules onto various alloy clusters (Ni_7V_2, Co_8V_2, $Ni_6Co_4V_3$, and $Ni_4Co_4V_4$). The B–H bond length, which is 1.210 Å in its free state, exhibits a significant increase across all systems, providing clear evidence of the onset of catalytic activation. Notably, in the $Ni_4Co_4V_4$ cluster, the B–H bond reaches a length of 1.312 Å (an elongation of +0.102 Å), suggesting that this synergistic framework is the most potent surface for borohydride dehydrogenation. Furthermore, the short distances observed between the Boron atom and the surface Vanadium sites (2.072 – 2.115 Å) confirm that V atoms serve as an 'anchor' during the reaction. This interaction stabilizes the BH_4^- molecule and facilitates the activation of the B–H bonds, thereby enhancing the overall catalytic efficiency.

Table 2. Structural Parameters Before and After BH_4^- Adsorption.

Cluster	dB−H (Free) (Å)	dB−H (Ads) (Å)	dM−V (Surface) (Å)	ΔdB−H (Elongation)	dB−V (Interaction)
Co_8V_2	1.210	1.282	2.512	+0.072	2.115
Ni_7V_2	1.210	1.305	2.485	+0.095	2.085
$Ni_4Co_4V_4$	1.210	1.312	2.478	+0.102	2.072
$Ni_6Co_4V_3$	1.210	1.298	2.492	+0.088	2.094

These results demonstrate that Ni–Co–V alloys exhibit a high catalytic potential for BH_4^- activation, in terms of both electronic energy levels and molecular orbital properties. This theoretical insight is further supported by experimental studies in the literature. For instance, Li et al. (2022) reported that a Ni–Co–V@PrGO (partially reduced graphene oxide) supported multimetal oxide catalyst exhibited excellent performance in overall water splitting, achieving low overpotentials (<150 mV) and small Tafel slopes (<70 mV/dec). Although their study highlighted the positive role of vanadium in enhancing surface morphology and electron transport, the investigated system was an oxide-phase catalyst with a different Ni:Co:V ratio and was applied to water electrolysis rather than borohydride hydrolysis. In contrast, the present study employs metallic Ni–Co–V clusters with tailored atomic compositions to provide a theoretical insight into their electronic and catalytic properties in $NaBH_4$ hydrolysis.

Similarly, Didehban et al. (2018) demonstrated that Co–Ni bimetallic nanocatalysts achieved approximately 40% higher hydrogen generation rates in $NaBH_4$ hydrolysis compared to monometallic counterparts. These experimental findings align well with the DFT results of this study, especially for the $Ni_6Co_4V_3$ and Ni_7V_2 clusters, which exhibit the lowest HOMO–LUMO gaps and the most favorable electron density distributions.

The presence of negatively charged regions on Ni-rich surfaces enhances the electrostatic attraction toward BH_4^- ions, thereby facilitating their adsorption and subsequent activation. This behavior is clearly reflected in the reduced HOMO–LUMO gaps and the increased thermodynamic stabilization observed for Ni-containing clusters, particularly $Ni_4Co_4V_4$ and Ni_7V_2. In contrast, Co-dominant systems tend to generate more localized electronic environments, leading to comparatively less delocalized charge transfer upon adsorption. Vanadium atoms, maintaining a positive charge character, act as effective electron-accepting centers and promote redox-assisted activation of the borohydride species. Consequently, Ni–Co–V clusters benefit from multipoint metal–ligand interactions, where Ni provides electron-rich adsorption sites, V facilitates charge acceptance, and Co contributes to structural and spin-related modulation, resulting in enhanced catalytic activity. The consistency between these theoretical trends and experimental observations further supports the reliability and predictive capability of the DFT-based models employed in this study.

The adsorption mechanism of $NaBH_4$ hydrolysis on trimetallic Ni–Co–V surfaces initiates with the electrostatic attraction of the BH_4^- ion toward electron-rich regions of the metal cluster. Density functional theory results indicate that Ni-dominant surface sites, characterized by relatively negative atomic charges, provide the primary adsorption centers for BH_4^-. This initial interaction is governed by charge-driven adsorption rather than direct bond cleavage and leads to a stable surface-bound borohydride configuration.

Upon adsorption, BH_4^- undergoes activation through coordinative interactions between its B–H bonds and adjacent Ni and Co atoms. This interaction induces elongation and polarization of the B–H bonds, accompanied by partial electron transfer from the borohydride moiety to low-lying metal-centered unoccupied states. As a result, the hydride character of BH_4^- is progressively weakened, rendering the adsorbed species more susceptible to subsequent reaction steps.

Water molecules preferentially interact with vanadium-enriched regions of the surface, where V atoms act as electron-deficient centers that stabilize incoming polar species. These water molecules do not dissociate immediately; instead, they form hydrogen-bonded configurations in proximity to the activated borohydride. The presence of vanadium facilitates proton transfer from water to the adsorbed BH_4^- through electrostatic stabilization of the developing charge asymmetry, lowering the energetic cost of proton–hydride coupling.

Rather than direct molecular hydrogen formation in a single step, the mechanism proceeds via stepwise dehydrogenation of the adsorbed borohydride species. Each proton transfer event is accompanied by electron redistribution across the Ni–Co–V framework, ultimately enabling the formation and desorption of H_2 molecules from the surface. Over the complete reaction pathway, BH_4^- is sequentially converted into boron-containing intermediates, releasing a total of four equivalents of hydrogen.

Throughout the adsorption and activation process, Ni atoms function primarily as electron-rich anchoring sites, Co atoms contribute to electronic flexibility and orbital overlap, and V atoms stabilize polar intermediates and proton-transfer configurations. This synergistic interplay between the three metals ensures effective adsorption, controlled bond activation, and stabilization of key intermediates, collectively enabling an efficient $NaBH_4$ hydrolysis process with reduced energetic barriers.

4. Conclusion

In this work, density functional theory calculations were employed to elucidate the role of alloy composition in governing the electronic properties and adsorption behavior of Ni–Co–V metal clusters toward $NaBH_4$ activation. The results clearly demonstrate that the incorporation of different transition metals enables systematic tuning of the electronic structure, as reflected by variations in HOMO–LUMO gaps and adsorption energies.

Ni-rich clusters exhibit enhanced electronic flexibility, characterized by relatively narrow HOMO–LUMO gaps, which favors charge redistribution upon interaction with $NaBH_4$-derived species. In particular, the $Ni_4Co_4V_4$ cluster emerges as the most balanced system, combining strong adsorption strength with moderate electronic stabilization upon complex formation. Structural and charge analyses indicate effective metal–hydride interactions, suggesting facilitated borohydride activation without excessive electronic destabilization of the cluster framework.

Although explicit reaction pathways and transition-state calculations were beyond the scope of the present study, the observed trends in electronic descriptors, adsorption energetics, and bond activation collectively indicate that Ni–Co–V alloy clusters provide a favorable platform for $NaBH_4$ activation. These findings highlight the importance of compositional synergy in multimetallic catalysts and provide a rational basis for future mechanistic investigations of hydrogen evolution from borohydride systems under aqueous conditions.

Conflict of Interest Statement

The author declares that there is no conflict of interest.

Research and Publication Ethics Statement

The author of this article declares that they have adhered to research and publication ethics in their work.

Ethics Committee Statement

The author of this article declares that the materials and methods used in this study did not require ethics committee approval and/or any legal or special permission.

Access to Data Used

The data generated in this study has not been made available in a database.

Use of Artificial Intelligence

The author declares that they did not use any kind of generative artificial intelligence in the writing of this article, in the creation of visuals, graphs, tables, or their corresponding headings.

References

Abhishek, B., Jayarama, A., Rao, A. S., Nagarkar, S. S., Dutta, A., Duttagupta, S. P., Prabhu, Duttagupta, S. P., & Pinto, R. (2024). Challenges in photocatalytic hydrogen evolution: Importance of photocatalysts and photocatalytic reactors. *International Journal of Hydrogen Energy, 81*, 1442–1466. https://doi.org/10.1016/j.ijhydene.2024.07.262

Akbaş, N. K., & Kutlu, B. (2022). Effect of hydroxyl (·OH) radicals on the progression of $NaBH_4$ hydrolysis reaction on fcc-Co surfaces: A DFT study. *Physica B: Condensed Matter, 647*, 414385. https://doi.org/10.1016/j.physb.2022.414385

Akkus, M. S. (2022). KBH_4 hidrolizinde ince film nikel katalizörünü kullanarak hidrojen üretimi ve proses optimizasyonu. *Niğde Ömer Halisdemir Üniversitesi Mühendislik Bilimleri Dergisi, 11*, 1097–1102. https://doi.org/10.28948/ngmuh.1143291

Akkus, M. S. (2023). The catalytic performance of nanorod nickel catalyst in the hydrolysis of lithium borohydride and dimethylamine borane. *Catalysts, 13*, 458. https://doi.org/10.3390/catal13030458

Altaf, C. T., Colak, T. O., Minkina, V. G., Shabunya, S. I., Sankir, M., Sankir N., Kalinin, V. (2023). Effect of titanium dioxide support for cobalt nanoparticle catalysts for hydrogen generation from sodium borohydride hydrolysis. *Catalysis Letters, 153*, 3136–3147. https://doi.org/10.1007/s10562-022-04215-9

Bampaou, M., & Panopoulos, K. D. (2025). An overview of hydrogen valleys: Current status, challenges and their role in increased renewable energy penetration. *Renewable and Sustainable Energy Reviews, 207*, 114923. https://doi.org/10.1016/j.rser.2024.114923

Bhandari, R., & Adhikari, N. (2024). A comprehensive review on the role of hydrogen in renewable energy systems. *International Journal of Hydrogen Energy, 82*, 923–951. https://doi.org/10.1016/j.ijhydene.2024.08.004

Caputo, R., & Tekin, A. (2011). Ab-initio crystal structure prediction. A case study: $NaBH_4$. *Journal of Solid State Chemistry, 184*, 1622–1630. https://doi.org/10.1016/j.jssc.2011.05.006

Cheng, L., Ferguson, G. A., Zygmunt, S. A., Curtiss, L. A. (2013). Structure–activity relationships for propane oxidative dehydrogenation by anatase-supported vanadium oxide monomers and dimers. *Journal of Catalysis, 302,* 31–36. https://doi.org/10.1016/j.jcat.2013.02.012

Clemmer, R. M., & Corbin, S. F. (2009). The influence of pore and Ni morphology on the electrical conductivity of porous Ni/YSZ composite anodes for SOFC applications. *Solid State Ionics, 180,* 721–730. https://doi.org/10.1016/j.ssi.2009.02.030

Dhanalakshmi, G., & Ravichandran, V. (2023). Synthesis of nanocrystalline nickel–iron alloys—A novel chemical reduction method. *Chemical Physics Impact, 6,* 100202. https://doi.org/10.1016/j.chphi.2023.100202

Didehban, A., Zabihi, M., & Shahrouzi, J. R. (2018). Experimental studies on the catalytic behavior of alloy and core–shell supported Co–Ni bimetallic nano-catalysts for hydrogen generation by hydrolysis of sodium borohydride. *International Journal of Hydrogen Energy, 43,* 20645–20660. https://doi.org/10.1016/j.ijhydene.2018.09.127

Do, Q. C., Kim, Y., Le, T. A., Kim, G. J., Kim, J., Kim, T., Lee, Y., Chae, H. (2022). Facile one-pot synthesis of Ni-based catalysts by cation–anion double hydrolysis method as highly active Ru-free catalysts for green H_2 production via NH_3 decomposition. *Applied Catalysis B: Environment and Energy, 307,* 121167. https://doi.org/10.1016/j.apcatb.2022.121167

Dragan, M. (2022). Hydrogen storage in complex metal hydrides $NaBH_4$: Hydrolysis reaction and experimental strategies. *Catalysts, 12,* 356. https://doi.org/10.3390/catal12040356

Duan, X., Kang, J., Tian, W., Zhang, H., Ho, S., Zhu, Y., Ao, Z., Sun, H., Wang, S. (2019). Interfacial-engineered cobalt@carbon hybrids for synergistically boosted evolution of sulfate radicals toward green oxidation. *Applied Catalysis B: Environmental, 256,* 117795. https://doi.org/10.1016/j.apcatb.2019.117795

Ecer, Ü., Zengin, A., & Şahan, T. (2023). Hydrogen generation from $NaBH_4$ hydrolysis catalyzed by cobalt(0)-deposited cross-linked polymer brushes: Optimization with an experimental design approach. *International Journal of Hydrogen Energy, 48,* 12814–12825. https://doi.org/10.1016/j.ijhydene.2022.12.224

Endrődi, B., Smulders, V., Simic, N., Wildlock, M., Mul, G., Mei, B., Cornell, A. (2019). In situ formed vanadium-oxide cathode coatings for selective hydrogen production. *Applied Catalysis B: Environmental, 244,* 233–239. https://doi.org/10.1016/j.apcatb.2018.11.038

Karaman, O. (2022). Three-dimensional graphene network supported Ni–Co bimetallic alloy nanocatalyst for hydrogen production by $NaBH_4$ hydrolysis and ANN modeling. *Chemical Engineering Research and Design, 181,* 321–330. https://doi.org/10.1016/j.cherd.2022.03.028

Koch, D., & Manzhos, S. (2019). Ab initio modeling and design of vanadia-based electrode materials for post-lithium batteries. *Journal of Physics D: Applied Physics, 53,* 083001. https://doi.org/10.1088/1361-6463/ab4ca0

Kuzmin, A. V., & Shainyan, B. A. (2023). Exploring catalytic ORR activity of V/Nb-doped, N-codoped CNT lattice carbons by DFT. *International Journal of Quantum Chemistry, 123,* e27017. https://doi.org/10.1002/qua.27017

Le, T. T., Sharma, P., Bora, B. J., Tran, V., Truong, T. H., Le, H., Nguyen, P. Q. (2024). Fueling the future: A comprehensive review of hydrogen energy systems and their challenges. *International Journal of Hydrogen Energy, 54,* 791–816. https://doi.org/10.1016/j.ijhydene.2023.08.044

Li, P., Yu, L., Matthews, M. A., et al. (2013). Deliquescence of $NaBH_4$ from density functional theory and experiments. *Industrial & Engineering Chemistry Research, 52,* 13849–13861. https://doi.org/10.1021/ie401742u

Li, Q., Zhang, X., Shen, J., Huang, Y., & Wu, H. (2022). Bifunctional keel flower-like Ni–Co–V multicomponent oxide catalyst with enhanced electron transport for accelerating overall water splitting. *Journal of Colloid and Interface Science, 628,* 467–476. https://doi.org/10.1016/j.jcis.2022.08.030

Loghmani, M. H., & Shojaei, A. F. (2013). Synthesis and characterization of Co–La–Zr–B quaternary amorphous nano-alloy: Kinetic study for hydrogen generation from $NaBH_4$ hydrolysis. *Journal of Alloys and Compounds, 580,* 61–66. https://doi.org/10.1016/j.jallcom.2013.05.078

Mirshafiee, F., & Rezaei, M. (2024). Synergistic catalytic performance of Co–Fe/CQD nanocatalyst for rapid hydrogen generation through $NaBH_4$ hydrolysis. *International Journal of Hydrogen Energy, 79,* 139–149. https://doi.org/10.1016/j.ijhydene.2024.07.011

Neese, F., Wennmohs, F., Becker, U., Riplinger, C. (2020). The ORCA quantum chemistry program package. *The Journal of Chemical Physics, 152,* 224108. https://doi.org/10.1063/5.0004608

Osman, A. I., Nasr, M., Eltaweil, A. S., Hosny, M., Farghali, M., Rooney, D., Monaem, E. (2014). Advances in hydrogen storage materials: Harnessing innovative technology, from machine learning to computational chemistry, for energy storage solutions. *International Journal of Hydrogen Energy, 67,* 1270–1294. https://doi.org/10.1016/j.ijhydene.2024.03.223

Petrova, V. V., Domnin, A. V., Porozov, Y. B., Kuliaev, P. O., Solovev, Y. V. (2024). Implementation of machine learning protocols to predict the hydrolysis reaction properties of organophosphorus substrates using descriptors of electron density topology. *Journal of Computational Chemistry, 45,* 170–182. https://doi.org/10.1002/jcc.27227

Qiao, Y., Liu, Q., Lu, S., Chen, G., Gao, S., Lu, W., Sun, X. (2020). High-performance non-enzymatic glucose detection using a conductive Ni-MOF electrocatalyst. *Journal of Materials Chemistry B, 8,* 5411–5415. https://doi.org/10.1039/D0TB00131G

Shen, T. F.-R., Lai, M.-H., Yang, T. C.-K., Fu, I., Liang, N., Chen W. (2012). Photocatalytic hydrogen production by vanadium oxides under visible light. *Journal of the Taiwan Institute of Chemical Engineers, 43,* 95–101. https://doi.org/10.1016/j.jtice.2011.06.004

Sun, L., Gao, X., Ning, X., Qiu, Z., Xing, L., Yang, H., Li, D., Dou, J., Meng, Y. (2023). Co–Ni bimetal carbon sphere catalysts for efficient $NaBH_4$ hydrolysis: The role of synergy and confine effect. *International Journal of Hydrogen Energy, 48,* 3413–3428. https://doi.org/10.1016/j.ijhydene.2022.10.2

Suzuki, Y., Kaneno, D., & Tomoda, S. (2009). Theoretical study on the mechanism and diastereoselectivity of $NaBH_4$ reduction. *The Journal of Physical Chemistry A, 113,* 2578–2584. https://doi.org/10.1021/jp809966u

Wu, L., Liao, M., Zhao, B., Li, Q.,Liu, B., Zhang, Y. (2023). Tuning the water-splitting mechanism on TiO_2 surfaces through hydroxylation. *Physical Chemistry Chemical Physics, 25,* 9264–9272. https://doi.org/10.1039/D2CP05457D